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(NAME OF DOCUMENT) SPECIFICATION

(TITLE OF THE INVENTION) ELECTROLESS Ni-B PLATING LIQUID,  
ELECTRONIC DEVICE AND METHOD FOR MANUFACTURING THE SAME

(CLAIMS)

5           (Claim 1) An electroless Ni-B plating liquid for forming  
a Ni-B alloy film on at least part of interconnects of an electronic  
device having an embedded interconnect structure, said  
electroless Ni-B plating liquid comprising nickel ions, a  
complexing agent for said nickel ions, an alkylamine borane or  
10 a hydrogen boride compound as a reducing agent for said nickel  
ions, and ammonia ions ( $\text{NH}_4^+$ ).

(Claim 2) The electroless Ni-B plating liquid according  
to claim 1, wherein a pH of said electroless Ni-B plating liquid  
is adjusted within the range from 8 to 12.

15           (Claim 3) The electroless Ni-B plating liquid according  
to claim 1 or 2, wherein said ammonia ions are prepared from ammonia  
water.

(Claim 4) An electronic device having an embedded  
interconnect structure of silver, silver alloy, copper or copper  
20 alloy, wherein a surface of an interconnect is selectively covered  
with a protective film of a Ni-B alloy film.

(Claim 5) A method for manufacturing an electronic device,  
comprising;

forming a protective film of a Ni-B alloy film selectively  
25 on a surface of an interconnect of an electronic device having  
an embedded interconnect structure by an electroless-plating  
process with use of an electroless Ni-B plating liquid according  
to any of claims 1 through 3.

(DETAILED DESCRIPTION OF THE INVENTION)

(0001)

(TECHNICAL FIELD TO WHICH THE INVENTION BELONGS)

The present invention relates to an electroless Ni-B plating  
5 liquid, an electronic device and a method for manufacturing the  
same. More particularly, the present invention relates to an  
electroless Ni-B plating liquid useful for forming a protective  
film for protecting the surfaces of the interconnects of an  
electronic device which has such an embedded interconnect  
10 structure that an electric conductor, such as silver or copper,  
is embedded in fine recesses for interconnects formed in the  
surface of a substrate such as a semiconductor substrate, and  
to an electronic device having the interconnects-protecting film  
formed by using the plating liquid, and a method for manufacturing  
15 the same.

(0002)

(PRIOR ART)

As a process for forming interconnects in an electronic  
device, the so-called "damascene process" which comprises filling  
20 trenches for interconnects and contact holes with a metal  
(electric conductor), is coming into practical use. According  
to this process, aluminum or, more recently a metal such as silver  
or copper, is filled into trenches for interconnects and contact  
holes previously formed in the interlevel dielectric of a  
25 semiconductor substrate. Thereafter, an extra metal is removed  
by chemical mechanical polishing (CMP) so as to flatten the surface  
of the substrate.

(0003)

In the case of interconnects formed by such a process, the embedded interconnects has exposed surfaces after the flattening processing. When an additional embedded interconnect structure is formed on such exposed surfaces of interconnects of a semiconductor substrate, the following problems may be encountered. For example, during the formation of a new  $\text{SiO}_2$  in the next interlevel dielectric forming process, the exposed surfaces of the pre-formed interconnects is likely to be oxidized. Further, upon etching of the  $\text{SiO}_2$  film for formation of via holes, the pre-formed interconnects exposed on the bottoms of via holes can be contaminated with an etchant, a peeled resist, etc.

(0004)

In order to avoid such problems, it has conventionally been performed to form an interconnect-protective film of  $\text{SiN}$  or the like not only on the interconnect region of a semiconductor substrate where the interconnects are exposed, but on the entire surface of the substrate, thereby preventing the contamination of the exposed interconnects with an etchant, etc.

(0005)

However, the provision of a protective film of  $\text{SiN}$  or the like on the entire surface of a semiconductor substrate, in an electronic device having an embedded interconnect structure, increases the dielectric constant of the interlevel dielectric, thus inducing delayed interconnection even when a low-resistance material such as silver or copper is employed as an interconnect material, whereby the performance of the electronic device may be impaired.

(0006)

In views of this, it may be considered to selectively cover the surfaces of the exposed interconnects with a Ni-B alloy film having a good adhesion to an interconnect material such as silver or copper and having a low resistivity ( $\rho$ ). A plated Ni-B film, 5 obtained by electroless Ni-B plating, is either a crystalline or an amorphous plated film depending on the boron content of the film. In this regard, a crystalline plated film is obtained when the boron content of the film is less than 10 at%, and an amorphous plated film is obtained when the boron content of the 10 film is 10 at% or more, generally.

(0007)

When a plated Ni-B film is used for the purpose of protecting the interconnects of an electronic device having an embedded interconnect structure, the plated film is required to be 15 thermally stable. From this point of view, it is necessary to use a crystalline plated film having a boron content of less than 10 at%. This is because a crystalline plated Ni-B film maintains its crystallinity after a heat treatment, whereas an amorphous Ni-B plated film forms a Ni-B compound upon the heat treatment 20 and thus becomes an unstable film.

(0008)

(PROBLEM TO BE SOLVED BY THE INVENTION)

However, when an intended Ni-B film, for the purpose of protecting the interconnects of an electronic device having an 25 embedded interconnect structure, is formed by electroless plating by using a plating liquid that is formulated to provide a plated film having a lowered boron content, the plating rate is likely to become too high to make a proper control of the process.



(0009)

In this regard, in electroless plating, the reaction time is equal to the solid-liquid contact time between the plating liquid and an object to be plated. Further, a plated Ni-B film  
5 to be used for protecting the interconnects of an electronic device must be as thin as several tens to several hundreds nm, for example. Accordingly, an enhanced plating rate makes the process control more difficult.

(0010)

10 The present invention has been made in view of the above situation in the related art. It is therefore an object of the present invention to provide an electroless Ni-B plating liquid which can lower the boron content of the resulting plated film without increasing the plating rate and form a Ni-B alloy film  
15 having an FCC crystalline structure, and also to provide an electronic device in which the interconnects are protected with the plated film formed by electroless plating carried out by using the plating liquid, and a method for manufacturing the same.

(0012)

20 (MEANS FOR SOLVING THE PROBLEMS)

According to the present invention defined in claim 1, there is provided an electroless Ni-B plating liquid for forming a Ni-B alloy film on at least part of interconnects of an electronic device having an embedded interconnect structure, said  
25 electroless Ni-B plating liquid comprising nickel ions, a complexing agent for said nickel ions, an alkylamine borane or a hydrogen boride compound as a reducing agent for said nickel ions, and ammonia ions ( $\text{NH}_4^+$ ).

(0013)

The inclusion of ammonia ions ( $\text{NH}_4^+$ ) in the plating liquid can lower the boron content of the plated film to provide a Ni-B alloy film having an FCC crystalline structure, and can also lower the plating rate by ammonia ions ( $\text{NH}_4^+$ ) so as to thereby facilitate the process control. It is considered, in this regard, that an ammonia ion, due to its generally high chelating force, may form a complex with a nickel ion to thereby lower the plating rate. Specific examples of the alkylamine borane include dimethylamine borane, diethylamine borane and trimethylamine borane.  $\text{NaBH}_4$  may be mentioned as a specific example of the hydrogen boride compound.

(0013)

According to the present invention defined in claim 2, the electroless Ni-B plating liquid according to claim 1, wherein a pH of the electroless Ni-B plating liquid is adjusted within the range from 8 to 12. By thus increasing the pH of the plating liquid to 8-12, it becomes possible to lower the boron content of the plated film and form a Ni-B alloy film having an FCC crystalline structure. The pH of the plating liquid is preferably 9-12, more preferably 10-12.

(0014)

According to the present invention defined in claim 3, the electroless Ni-B plating liquid according to claim 1 or 2, wherein the ammonia ions are prepared from ammonia water.

(0015)

According to the present invention defined in claim 4, there is provided an electronic device having an embedded interconnect

structure of silver, silver alloy, copper or copper alloy, wherein a surface of an interconnect is selectively covered with a protective film of a Ni-B alloy film.

(0016)

5 By thus selectively covering the surfaces of the interconnects and protecting the interconnects with the protective film of a Ni-B alloy film that has a high adhesion to silver or copper and has a low resistivity ( $\rho$ ), an increase in the dielectric constant of the interlevel dielectric of an  
10 electronic device having an embedded interconnect structure can be suppressed. Further, the use as an interconnect material of a low-resistance material, such as silver or copper, can attain speedup and densification of the electronic device.

(0017)

15 According to the present invention defined in claim 5, there is provided a method for manufacturing an electronic device, comprising; forming a protective film of a Ni-B alloy film selectively on a surface of an interconnect of an electronic device having an embedded interconnect structure by an  
20 electroless-plating process with use of an electroless Ni-B plating liquid according any to claim 1 through 3.

(0018)

Plating with an electroless Ni-B plating liquid containing an alkylamine borane or a hydrogen boride compound as a reducing  
25 agent, e.g. an electroless Ni-B plating liquid containing as a reducing agent DMAB (dimethylamine borane) that causes an anodic oxidation reaction with silver, is known to be effected selectively onto silver or copper. Thus, by immersing the

substrate of an electronic device having exposed surfaces of interconnects in the plating liquid, plating is effected selectively onto the exposed surfaces of interconnects.

(0019)

5 (EMBODIMENTS OF THE INVENTION)

Preferred embodiments of the present invention will now be described with reference to the drawings.

FIG. 1 illustrates, in a sequence of process steps, an example of forming silver interconnects in an electronic device according to the present invention. As shown in FIG. 1(a), an insulating film 2 of  $\text{SiO}_2$  is deposited on a conductive layer 1a in which electronic devices are formed, which is formed on an electronic device substrate 1. A contact hole 3 and a trench 4 for interconnects are formed in the insulating film 2 by the lithography/etching technique. Thereafter, a barrier layer 5 of TaN or the like is formed on the entire surface, and a copper seed layer 6 as an electric supply layer for electroplating is formed on the barrier layer 5 by sputtering or the like.

(0020)

20 Then, as shown in FIG. 1(b), silver plating is performed onto the surface of the electronic device substrate 1 to fill the contact hole 3 and the trench 4 with silver and, at the same time, deposit a silver layer 7 on the insulating film 2. Thereafter, the silver layer 7 on the insulating film 2 is removed by chemical mechanical polishing (CMP) so as to make the surface of the silver layer 7 filled in the contact hole 3 and the trench 4 for interconnects and the surface of the insulating film 2 lie substantially on the same plane. Interconnects 8 composed of

the copper seed layer 6 and the silver layer 7, as shown in FIG. 1(c), are thus formed in the insulating layer 2.

(0021)

Next, electroless Ni-B plating is performed onto the surface of the substrate 1 to selectively form a protective film 9 composed of a Ni-B alloy film of an FCC crystalline structure, having a boron content of 0.01 at% - 10 at%, on the exposed surfaces of the interconnects 8, thereby protecting the interconnects 8. The thickness of the protective film 9 is generally 0.1-500 nm, preferably 1-200 nm, and more preferably 10-100 nm.

(0022)

The protective film 9 is formed selectively on the exposed surfaces of the interconnects 8 by using an electroless Ni-B plating liquid containing nickel ions, a complexing agent for nickel ions, an alkylamine borane or a hydrogen boride compound as a reducing agent for nickel ions, and ammonia ions ( $\text{NH}_4^+$ ), a pH of the plating liquid being adjusted to e.g. 8-12, and dipping the surface of the substrate 1 in the plating liquid.

(0023)

The protection of the interconnects 8 by the provision of the protective film 9 can prevent, in forming thereon an additional embedded interconnect structure, the oxidation of the surfaces of the interconnects during formation of a new  $\text{SiO}_2$  in the next interlevel dielectric forming process, and the contamination of the interconnects with an etchant or a peeled resist upon etching of the  $\text{SiO}_2$  film.

(0024)

Further, by selectively covering the surfaces of the

interconnects 8 and protecting the interconnects 8 with the protective film 9 of a Ni-B alloy film that has a high adhesion to silver as an interconnect material and has a low resistivity ( $\rho$ ), an increase in the dielectric constant of the interlevel dielectric of an electronic device having an embedded interconnect structure can be suppressed. Further, the use of as an interconnect material of silver, which is a low-resistance material, can attain speedup and densification of the electronic device.

10 (0025)

Though this example shows the use of silver as an interconnect material, a silver alloy, copper or a copper alloy may also be used.

(0026)

15 In performing a CMP treatment onto the surface of the substrate 1 in which the silver layer is filled, there is a case where in a relatively wide trench for interconnects, the surface of the interconnects 8 composed of the copper seed layer 6 and the silver layer 7 is dished, as shown in FIG. 8. When electroless  
20 Ni-B plating is performed onto such a dished surface of the interconnects 8, the dished space is filled with the protective film 9 composed of the Ni-B alloy film, whereby the interconnects 8 can be prevented from being exposed.

(0027)

25 The present plating liquid for use in the electroless Ni-B plating will now be described in detail below. The present plating liquid is characterized in that a pH of the plating liquid is adjusted to 8-12 by using ammonia water, thereby controlling the

boron content of the protective film 9 (plated film) to less than 10 at% to provide the protective film 9 with an FCC crystalline structure, and lowering the plating rate.

(0028)

5 First, a first plating liquid (the present plating liquid) was prepared by using, as shown in Table 1 below, 0.02 M of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  as a supply source of divalent nickel ions, 0.02 M of DL-malic acid and 0.03 M of glycine as complexing agents for nickel ions, and 0.02 M of DMAB (dimethylamine borane) as a reducing agent  
10 for nickel ions, and by adjusting the pH of the plating liquid to 5-12 by using ammonia water. Further, a second plating liquid was prepared in the same manner as in the first plating liquid (the present plating liquid), except that the pH of the plating liquid is adjusted to 5-12 by using, instead of ammonia water,  
15 TMAH (tetramethylammonium hydroxide) which is widely used as a pH adjusting agent.

(Table 1)

	First plating liquid (the present plating liquid)	Second plating liquid
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.02 M	0.02 M
DMAB	0.02 M	0.02 M
DL-malic acid	0.02 M	0.02 M
Glycine	0.03 M	0.03 M
PH	pH = 5 - 12 with ammonia water	pH = 5 - 12 with TMAH

Temperature	60°C	60°C
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(0029)

Using the first plating liquid (the present plating liquid) and the second plating liquid, electroless Ni-B plating was performed onto a semiconductor wafer on which a barrier layer (Ta<sub>2</sub>N<sub>5</sub>, 20 nm) and a copper film (copper, 100 nm) had been formed by sputtering. By varying the pHs of the respective plating liquids within the pH range of 5-12, the relationship between pH of plating liquid and electroless Ni-B plating rate, and between pH of plating liquid and B (boron) content of plated film was determined, the results of which are shown in FIGS. 2 and 3.

(0030)

As can be seen from FIG. 2, with respect to the electroless Ni-B plating liquid (first plating liquid) in which the pH is adjusted with ammonia water, the plating rate drastically decreases when the pH exceeds 8, and lowers down to below 100 nm/min in a pH range of 9-12. Further, a Ni-B alloy film having a boron content of less than 10 at% can be obtained when the pH of the plating liquid increases to 8 or more.

(0031)

In contrast, it is apparent from FIG. 3 that in the case of the electroless Ni-B plating liquid (second plating liquid) in which the pH is adjusted with TMAH, though a Ni-B alloy film having a boron content of less than 10 at% may be obtained at a pH exceeding 9, the plating rate increases with an increase in pH and reaches to a considerably high level at a pH exceeding 9.



(0032)

The above results show that it is preferred to use, as a plating liquid for forming a interconnect-protective film of Ni-B alloy film in an electronic device having an embedded interconnect structure, an electroless Ni-B plating liquid whose pH is adjusted to 8-12, preferably 9-12, more preferably 10-12, by using ammonia water.

(0033)

Next, a third plating liquid (the present plating liquid) was prepared by using, as shown in Table 2 below, 0.02 M of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  as a supply source of divalent nickel ions, 0.02 M of DL-malic acid and 0.03 M of glycine as complexing agents for nickel ions, and 0.02 M of DMAB (dimethylamine borane) as a reducing agent for nickel ions, and by adjusting a pH of the plating liquid to 10 with ammonia water and adjusting the temperature of the plating liquid to 60°C.

(Table 2)

	Third plating liquid (the present plating liquid)
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.02 M
DMAB	0.02 M
DL-malic acid	0.02 M
Glycine	0.03 M
pH	pH = 10 with ammonia water
Temperature	60°C

20

(0034)

Using the third plating liquid (the present plating liquid), electroless plating was performed onto an electronic device substrate (semiconductor wafer) on which a barrier layer (Ta<sub>2</sub>N<sub>5</sub>, 20 nm) and a copper layer (copper, 600 nm) had been formed by sputtering. The Ni-B alloy film thus formed on the substrate had a thickness of 40 nm and a boron content of 4.2 at%. The Ni-B alloy film was examined on its oxidation resistance. The results are shown in Table 3.

(Table 3)

	Sheet resistance (m $\Omega$ /sq)
After plating	30.5
After atmospheric heat treatment	28.7
After O <sub>2</sub> plasma ashing	30.1

Atmospheric heat treatment: in air, hot plate, 200°C, 30 min  
O<sub>2</sub> plasma ashing: 1Torr, 800W, 250°C, 30 min.

(0035)

As apparent from the results of Table 3, there is no substantial change in the sheet resistance after either of the oxidizing treatments, indicating good oxidation resistance of the Ni-B alloy film. This shows that the third plating liquid (the present plating liquid) is suited for use as an electroless Ni-B plating liquid for forming an interconnect-protecting film of Ni-B alloy film in an electronic device having an embedded interconnect structure.

(0036)

Next, using the third plating liquid (the present plating liquid) having the composition shown in Table 2, electroless plating was performed onto a substrate in which, after forming

by sputtering a barrier layer (TiN, 50 nm) and a seed layer (copper, 100 nm) on a semiconductor wafer, a plated Ag film of 500 nm-thickness had been formed by using an electrolytic Ag plating liquid [ $\text{KAg}(\text{CN})_2$ : 0.03 M, KCN: 0.23 M, pH=11, liquid temp. 25°C] and using a pulse system [pulse current density: 10 mA/cm<sup>2</sup>, voltage application time: 1 msec, and pause time: 10 msec]. The Ni-B alloy film was analyzed by X-ray diffractometry. The Ni-B alloy film thus formed on the substrate had a thickness of 40 nm and a boron content of 4.2 at%. For comparison, two Ni-B alloy films having a boron content of 13.5 at% and of 20 at%, obtained by using commercial electroless Ni-B plating liquids, were also analyzed by X-ray diffractometry. To the respective samples, heat treatment (annealing) was conducted by introducing the substrate after the electroless plating into a quartz furnace, exhausting the air in the furnace to  $1 \times 10^{-5}$  Torr, introducing a high-purity Ar gas into the furnace, and then heating the substrate at 400°C for one hour. The X-ray diffraction analysis was conducted on each sample before and after the annealing.

(0037)

FIGS. 4(a) and 5(a) show the X-ray diffraction patterns of the Ni-B alloy film having a boron content of 4.2 at%, before and after the annealing, obtained by using the third plating liquid (the present plating liquid); FIGS. 4(b) and 5B show the X-ray diffraction patterns of the Ni-B alloy film having a boron content of 13.5 at%, before and after the annealing, obtained by using the commercial plating liquid; and FIGS. 4(c) and 5(c) show the X-ray diffraction patterns of the Ni-B alloy film having a boron content of 20 at%, before and after the annealing, obtained by

using the commercial plating liquid.

(0038)

It is apparent from these Figures that the Ni-B alloy film having a boron content of 4.2 at%, obtained by using the third plating liquid (the present plating liquid), has an FCC crystalline structure, both before and after the annealing, whereas the Ni-B alloy films having a boron content of 13.5 at% and of 20 at%, obtained by using the commercial plating liquids, are amorphous before the annealing, and become Ni + Ni<sub>3</sub>B (intermetallic compound) after the annealing.

(0039)

The X-ray diffraction data thus shows that the Ni-B alloy film obtained by using the third plating liquid (the present plating liquid) is thermally stable and can maintain the crystalline structure after undergoing a heat treatment. This indicates suitability of the present plating liquid for use as an electroless Ni-B plating liquid for forming an interconnect-protecting film of Ni-B alloy film in an electronic device having an embedded interconnect structure.

(0040)

Further, using the third plating liquid (the present plating liquid) having the composition shown in Table 2, electroless plating was performed onto a substrate in which, after forming by sputtering a barrier layer (TiN, 50 nm) and a seed layer (copper, 100 nm) on a electronic device substrate (semiconductor wafer), a plated Ag film of 500 nm-thickness had been formed by using an electrolytic Ag plating liquid [KAg(CN)<sub>2</sub>: 0.03 M, KCN: 0.23 M, pH=11, liquid temp. 25°C] and using a pulse system [pulse current

density: 10 mA/cm<sup>2</sup>, voltage application time: 1 msec, and pause time: 10 msec]. The Ni-B alloy film thus formed on the substrate had a thickness of 70 nm and a boron content of 4.8 at%. The Ni-B alloy film was examined on its barrier properties. For comparison, the barrier properties of a Ni-B alloy film having a thickness of 90 nm and a boron content of 14.5 at%, obtained by using a commercial electroless Ni-B plating liquid, was also examined.

(0041)

FIG. 6 shows a state of the Ni-B alloy film having a boron content of 4.8 at% obtained by using the third plating liquid (the present plating liquid). FIGS. 6(a) and 6(b) show the results of AES analysis in the depth direction of the Ni-B alloy film before and after the annealing; FIG. 6(c) shows the results of AES analysis of the surface of the annealed Ni-B alloy film. FIG. 7 shows a state of the Ni-B alloy film having a boron content of 14.5 at% obtained by the use of the commercial plating liquid. FIGS. 7(a) and 7(b) show the results of AES analysis in the depth direction of the Ni-B alloy film before and after the annealing; and FIG. 7(c) shows the results of AES analysis of the surface of the annealed Ni-B alloy film.

(0042)

As apparent from these Figures, in the case of the Ni-B alloy cover film having a boron content of 14.5 at%, obtained by using the third plating liquid (the present plating liquid), no copper diffusion is seen in the Ni-B alloy cover, indicating that the present Ni-B alloy film functions as an excellent barrier to copper diffusion.

(0043)

Further, a fourth plating liquid (the present plating liquid) was prepared by using, as shown in Table 4 below, 0.1 M of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  as a supply source of divalent nickel ions, 0.1 M of DL-malic acid and 0.15 M of glycine as complexing agents for nickel ions, and 0.1 M of DMAB (dimethylamine borane) as a reducing agent for nickel ions, and by adjusting the pH of the plating liquid to 5-10 with ammonia water and adjusting the temperature of the plating liquid to 50-90°C.

10 (Table 4)

	Fourth plating liquid (the present plating liquid)
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.1 M
DMBA	0.1 M
DL-malic acid	0.1 M
Glycine	0.15 M
pH	5-10
Temperature	50°C - 90°C

(0044)

Using the fourth plating liquid (the present plating liquid), electroless Ni-B plating was performed onto a sample (25 mm x 50 mm) in which a laminated film of Ti (20 nm) / TiN (70 nm) / Cu (200 nm) had been formed in this order by ordinary magnetron sputtering on a silicon substrate, and then a plated Ag film of 500 nm-thickness had been formed by using an electrolytic Ag plating liquid [ $\text{KAg}(\text{CN})_2$ : 0.03 M, KCN: 0.23 M, pH=11, liquid temp. 25°C] and using a pulse system [pulse current density: 10 mA/cm<sup>2</sup>, voltage application time: 1 msec, and pause time: 10 msec]. Next,

the sample after the Ni-B plating treatment was heat-treated (annealed) by introducing the sample into a quartz furnace, exhausting the air in the furnace to  $1 \times 10^{-5}$  Torr, introducing a high-purity Ar gas into the furnace, and then heating the sample at 400°C for one hour.

(0045)

Table 5, given below, and FIG. 9 show the relationship between pH of plating liquid and plating rate, and between pH of plating liquid and B (boron) content of plated film when the temperature of the plating liquid was made constant at 80°C while the pH was varied within the range of 5-10. Table 6, given below, and FIG. 10 show the relationship between temperature of plating liquid and plating rate, and between temperature of plating liquid and B (boron) content of plated film when the pH of the plating liquid was made constant at 10 while the temperature was varied within the range of 50-90°C. The measurement of the boron content of a plated film was conducted by dissolving and peeling the plated film with the use of 7N nitric acid, and subjecting the solution to ICP emission spectrophotometer.

(Table 5)

pH (-)	Plating rate (nm/min)	B content (at%)
5	310	13.5
6.2	500	12.2
8	430	5.5
10	160	2.7

Note: plating time: 1 min

plating liquid temp.: 80°C

(Table 6)

Temp. (°C)	Plating rate (nm/min)	B content (at%)
50	4	1.8
60	56	2.1
70	90	2.1
80	160	2.7
90	200	3

Note: plating time: 1 min

plating liquid pH: 10

5

(0046)

It has been reported that generally in electroless Ni-B plating, the plating rate tends to increase and the boron content of the plated film tends to decrease with an increase in the pH of the plating liquid. However, as shown in Table 5 and FIG. 9, when the pH is increased by using ammonia water, the boron content of the plated film shows a tendency to decrease and, when the pH exceeds 6-8, the plating rate also shows a tendency to decrease. When the pH is made constant at 10, as shown in Table 6 and FIG. 10, the plating rate shows a tendency to increase with an increase in the temperature of the plating liquid. The boron content of the plated film also shows a slight tendency to increase, but at a low level of less than 3 at% even at an elevated plating liquid temperature. FIG. 10 also shows that almost no reaction takes place at 50°C, whereas the plating rate reaches 200 nm/min at 90°C. Thus, the temperature of the plating liquid may be



adjusted within the range of 50-90°C, preferably 55-75°C.

(0047)

Further, in order to determine the stability (Cu barrier effect) of the Ni-B alloy film, the above sample after the heat treatment was analyzed in the depth direction and on the surface by auger electronic spectroscopy. For comparison, the same analysis was conducted on a Ni-B alloy film having a boron content of 13.5 at% obtained by using a commercial plating liquid. The results of the analysis are shown in Table 7.

10

(Table 7)

	Ni-B film thickness	B content	Cu barrier effect
The present plating liquid	150 nm	3.2 at%	Observed
Commercial plating liquid	300 nm	13.5 at%	Not observed

(0048)

As well be appreciated from the results of Table 7, the Ni-B alloy film having a boron content of 3.2 at% has a Cu diffusion-preventing effect, whereas the Ni-B alloy film having a boron content 13.5 at% has no Cu diffusion-preventing effect.

(0049)

Further, in order to analyze the structure of the Ni-B alloy film, X-ray diffraction analysis was conducted on the above sample, before and after the heat treatment. For comparison, the same analysis was conducted on the above comparative Ni-B alloy film having a boron content of 13.5 at%. The results are shown in

Table 8.

(Table 8)

	Ni-B film thickness	B content	After plating	After heat treatment
The present plating liquid	150 nm	3.2 at%	Ni (crystalline)	Ni (crystalline)
Commercial plating liquid	300 nm	13.5 at%	Amorphous	Ni + Ni <sub>3</sub> B

(0050)

5        The Ni-B alloy film having a boron content of 3.2 at% has  
a crystalline phase both before and after the heat treatment  
(annealing), whereas the Ni-B alloy film having a boron content  
of 13.5 at% is amorphous before the heat treatment, and becomes  
Ni + Ni<sub>3</sub>B (intermetallic compound) after the heat treatment. This  
10 indicates that a Ni-B alloy film of a smaller boron content can  
better maintain the crystalline phase and is more thermally  
stable.

(0051)

15        It is considered in this connection that the Ni-B having  
a boron content of 3.2 at% maintains its crystalline phase upon  
undergoing the heat environment, and boron segregated at a crystal  
grain boundary may prevent diffusion of copper through the grain  
boundary. In contrast, the Ni-B alloy film having a boron content  
of 13.5 at% makes a structural change upon the heat treatment  
20 (thermally unstable) to form the intermetallic compound which

is fragile, whereby diffusion of copper cannot be prevented.

(0052)

Next, a trial formation of a Ni-B alloy protective film on silver damascene interconnects was performed. FIGS. 11(a) and 11(b) are SEM photographs of the silver damascene interconnects (width:  $1\mu\text{m}$ , spacing:  $1\mu\text{m}$ , depth of trench:  $1\mu\text{m}$ ) formed in a silicon substrate; and FIGS. 12(a) and 12(b) are SEM photographs of the Ni-B alloy protective film formed on the silver damascene interconnects. As shown in these Figures, the Ni-B alloy film was formed selectively on the exposed surfaces of the silver damascene interconnects.

(0053)

The above described experimental results clearly show that the Ni-B alloy film having a boron content of 3.2 at%, obtained by using the electroless Ni-B plating liquid which contains ammonia ions, has a crystalline phase that is thermally stable, and can be suitably utilized as a protective film for multilayer silver interconnects having, for example, a laminated structure of Ti/TiN/Cu/Ag/Ni-B.

Though the above described examples show the use of the present Ni-B alloy film as a protective film, it may also be used as a barrier material since it has a copper diffusion-preventing effect.

(0054)

(EFFECTS OF THE INVENTION)

As described hereinabove, according to the present invention, the electroless Ni-B plating liquid can lower the boron content of the plated film without increasing the plating rate and form

a Ni-B alloy film having an FCC crystalline structure. By using the present plating liquid, which can facilitate the process control, a protective film of Ni-B alloy film can be formed selectively on the interconnects of an electronic device having an embedded interconnect structure. The present invention can thus contribute to speedup and densification in electronic devices.

(BRIEF DESCRIPTION OF THE DRAWINGS)

(Fig. 1)

FIGS. 1(a) through 1(c) are diagrams illustrating, in a sequence of process steps, an example of forming silver interconnects in an electronic device in accordance with the present invention.

(Fig. 2)

FIG. 2 is a graph showing the relationship between pH of plating liquid and electroless Ni-B plating rate, and between pH of plating liquid and B content of plated film when the pH of a plating liquid is adjusted with ammonia water.

(Fig. 3)

FIG. 3 is a graph showing the relationship between pH of plating liquid and electroless Ni-B plating rate and, between pH of plating liquid and B content of plated film when the pH of a plating liquid is adjusted with TMAH.

(Fig. 4)

FIG. 4(a) shows an X-ray diffraction pattern of a Ni-B alloy film having a boron content of 4.2 at%, before annealing, obtained by the use of the present plating liquid; FIG. 4(b) shows an X-ray diffraction pattern of a Ni-B alloy film having a boron content

of 13.5 at%, before annealing, obtained by the use of a commercial plating liquid; and FIG. 4(c) shows an X-ray diffraction pattern of a Ni-B alloy film having a boron content of 20 at%, before annealing, obtained by the use of a commercial plating liquid.

5 (Fig. 5)

FIG. 5(a) shows an X-ray diffraction pattern of a Ni-B alloy film having a boron content of 4.2 at%, after annealing, obtained by the use of the present plating liquid; FIG. 5(b) shows an X-ray diffraction pattern of a Ni-B alloy film having a boron content  
10 of 13.5 at%, after annealing, obtained by the use of a commercial plating liquid; and FIG. 5(c) shows an X-ray diffraction pattern of a Ni-B alloy film having a boron content of 20 at%, after annealing, obtained by the use of a commercial plating liquid.

(Fig. 6)

15 FIG. 6(a) is a chart showing the results of AES analysis in the depth direction of a Ni-B alloy film having a boron content of 4.8 at%, before annealing, obtained by the use of the present plating liquid; FIG. 6(b) is a chart showing the results of AES analysis in the depth direction of the Ni-B alloy film, but after  
20 annealing; and FIG. 6(c) is a chart showing the results of AES analysis of the surface of the annealed Ni-B alloy film.

(Fig. 7)

FIG. 7(a) is a chart showing the results of AES analysis in the depth direction a Ni-B alloy film having a boron content  
25 of 14.5 at%, before annealing, obtained by the use of a commercial plating liquid; FIG. 7(b) is a chart showing the results of AES analysis is the depth direction of the Ni-B alloy film, but after annealing; and FIG. 7(c) is a chart showing the results of AES

analysis of the surface of the annealed Ni-B alloy film.

(Fig. 8)

FIG. 8 is a cross-sectional diagram illustrating another example of forming a protective film in an electronic device in accordance with the present invention.

(Fig. 9)

FIG. 9 is a graph showing the relationship between pH of plating liquid and electroless Ni-B plating rate, and between pH of plating liquid and B content of plated film at a constant plating liquid temperature.

(Fig. 10)

FIG. 10 is a graph showing the relationship between temperature of plating liquid and electroless Ni-B plating rate and between temperature of plating liquid and B content of plated film at a constant plating liquid pH.

(Fig. 11)

FIGS. 11(a) and 11(b) are SEM photographs of silver damascene interconnects formed in a silver substrate.

(Fig. 12)

FIGS. 12(a) and 12(b) are SEM photographs of a Ni-B alloy protective film formed on the interconnects of FIGS. 11(a) and 11(b).

- 1 electronic device substrate
- 2 insulating film
- 25 3 contact hole
- 4 trench
- 5 barrier layer
- 6 copper seed layer

- 7 silver layer
- 8 interconnects
- 9 protective film (Ni-B alloy film)

(NAME OF DOCUMENT)

ABSTRACT

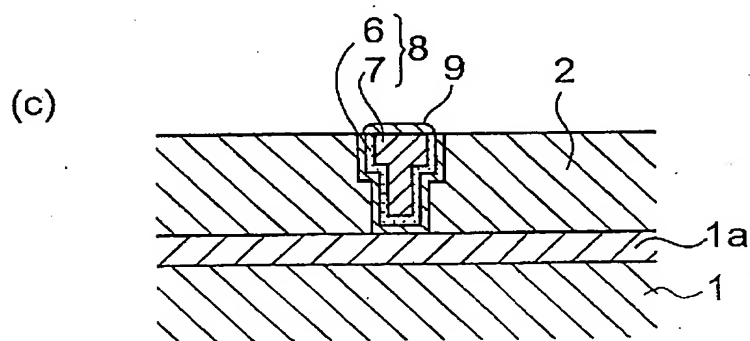
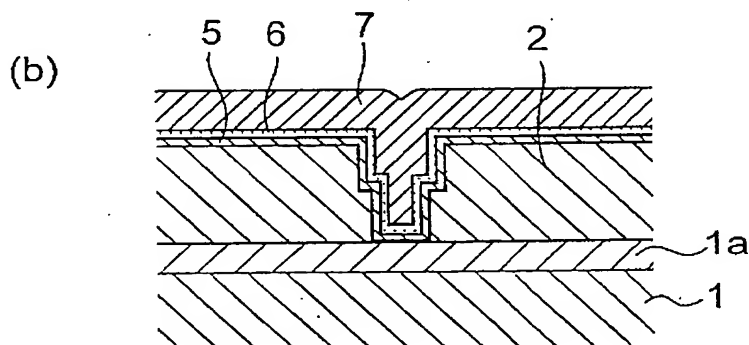
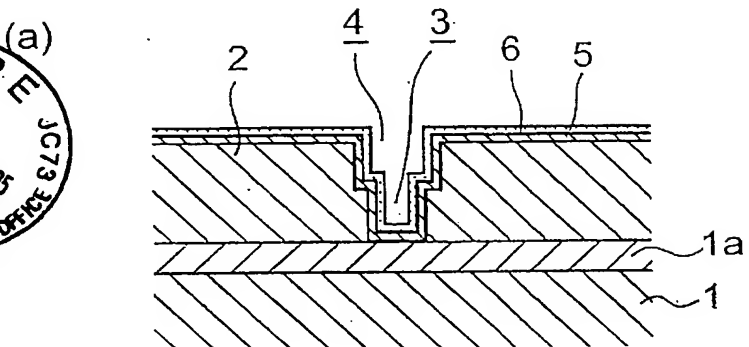
(ABSTRACT)

(PROBLEM)        The present invention provides an electroless Ni-B  
plating liquid which can lower the boron content of the resulting  
5 plated film without increasing the plating rate and form a Ni-B  
alloy film having an FCC crystalline structure.

(MEANS FOR RESOLUTION)    There is provided an electroless Ni-B  
plating liquid for forming, a Ni-B alloy film on at least part  
of the interconnects of an electronic device having an embedded  
10 interconnect structure, the electroless Ni-B plating liquid  
comprising nickel ions, a complexing agent for nickel ions, an  
alkylamine borane or a hydrogen boride compound as a reducing  
agent for nickel ions, and ammonia ions ( $\text{NH}_4^+$ ).

(Selected Figure) Fig. 1

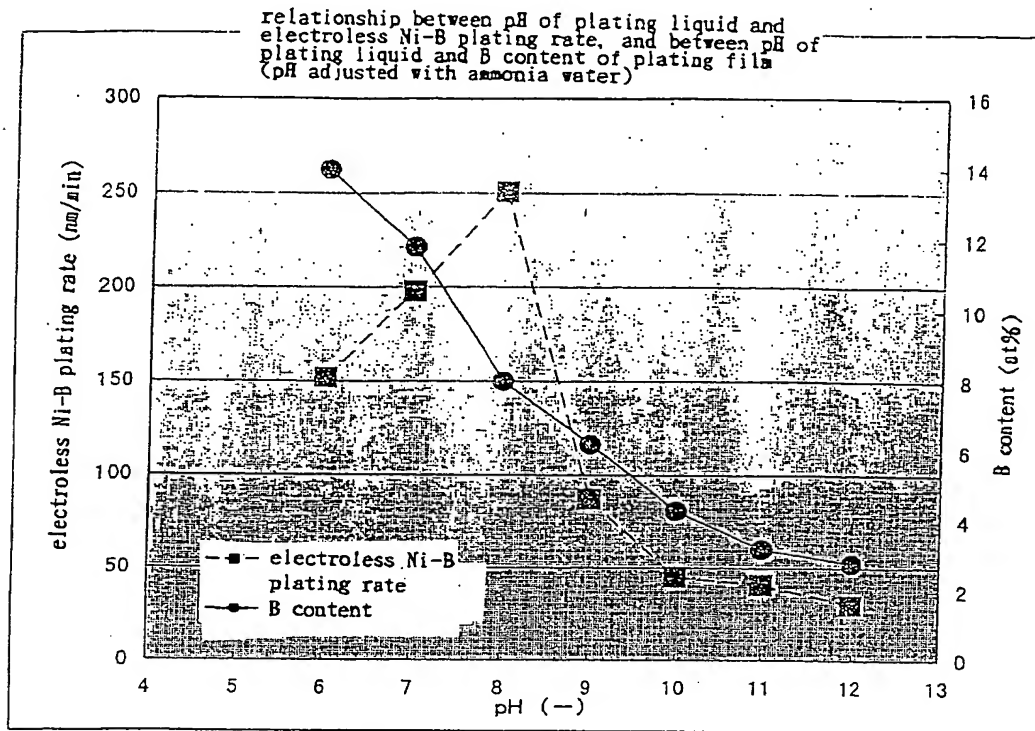




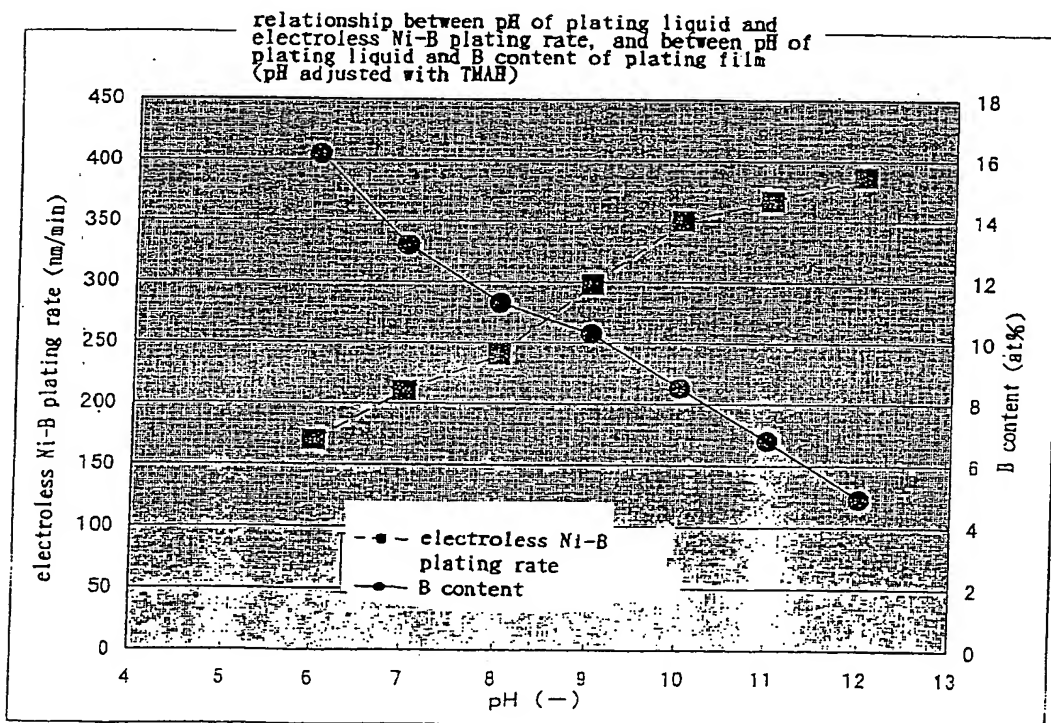
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(FIG. 2)



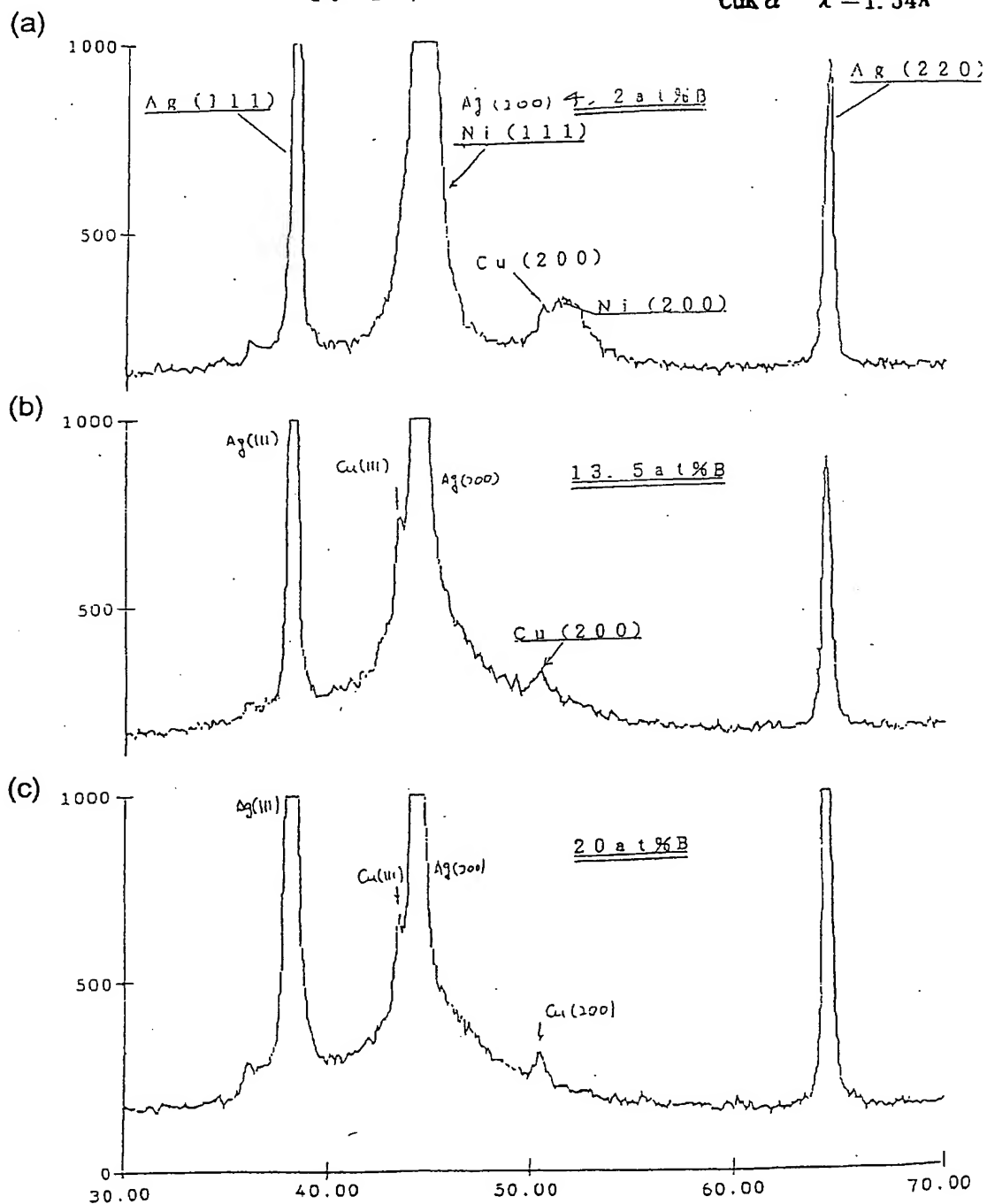
(FIG. 3)



X-ray diffractometry

Ni-B/Ag/Cu/TiN  
as depo

incidence angle for thin film  $5^\circ$   
 $\text{CuK}\alpha \quad \lambda = 1.54\text{\AA}$



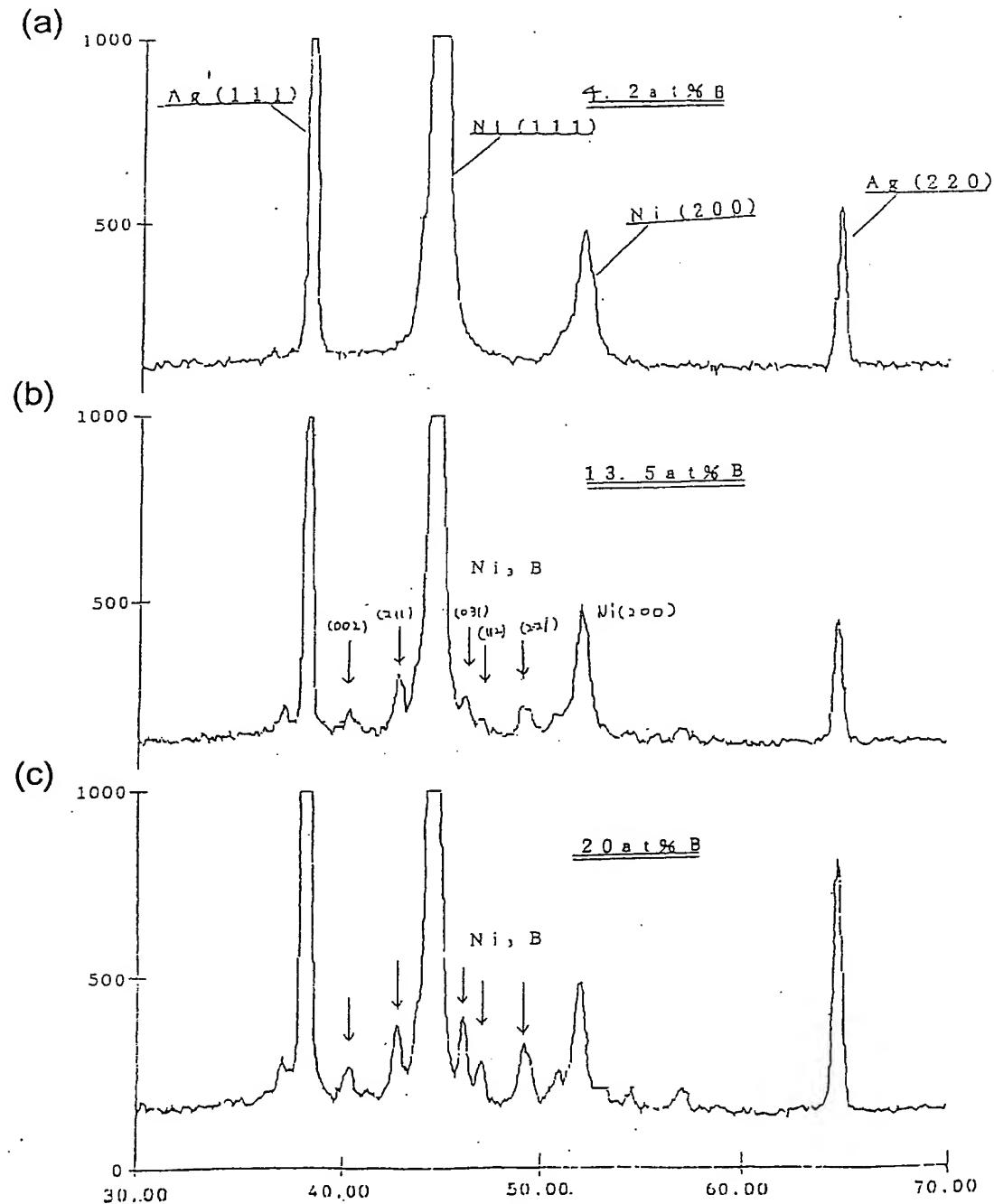
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 (FIG. 5)

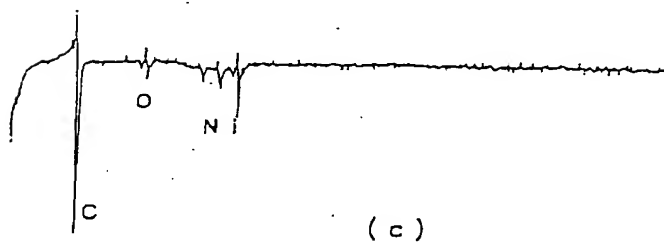
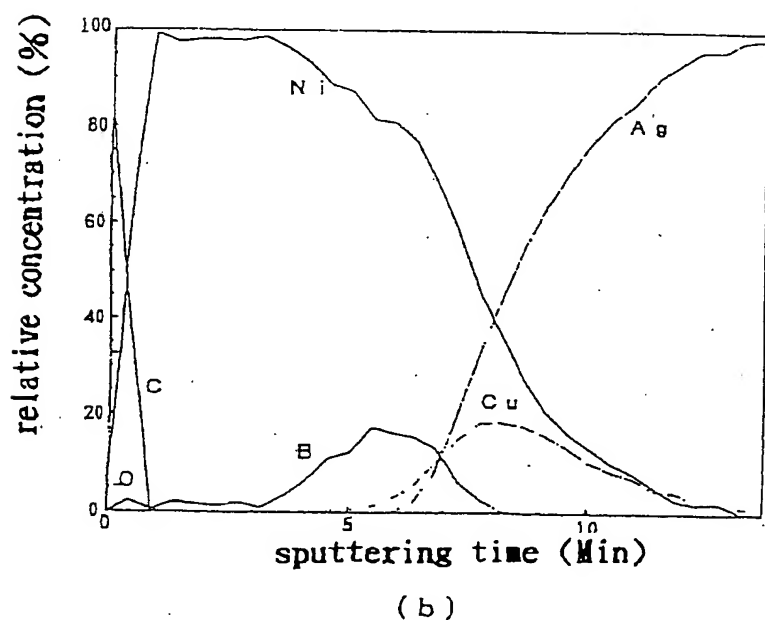
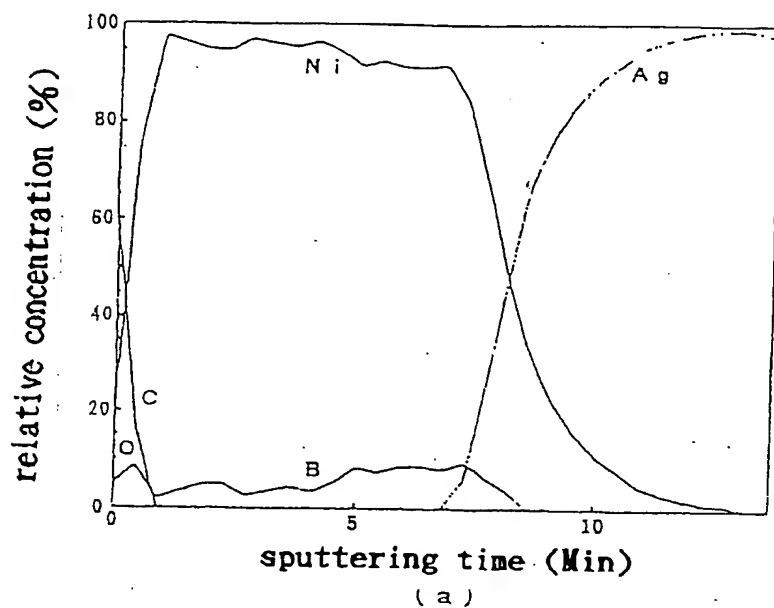
## X-ray diffractometry

Ni-B/Ag/Cu/TiN

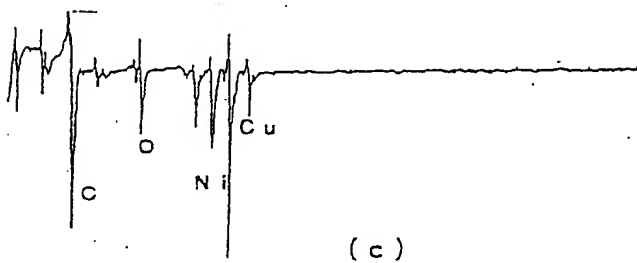
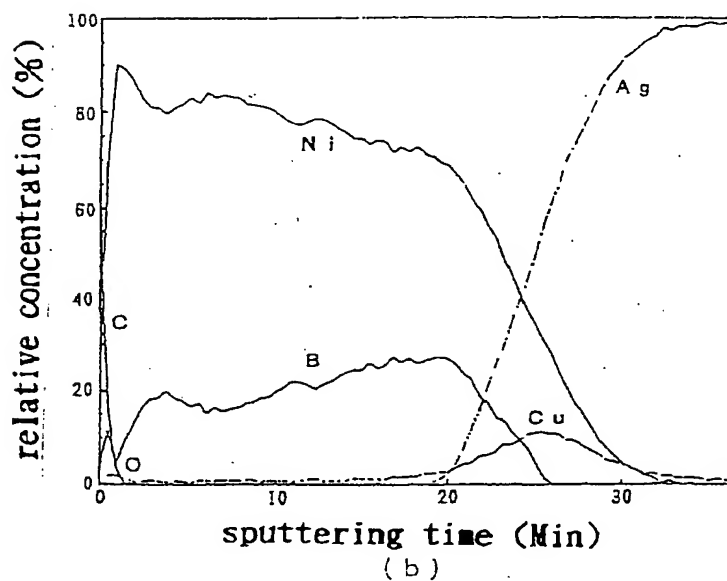
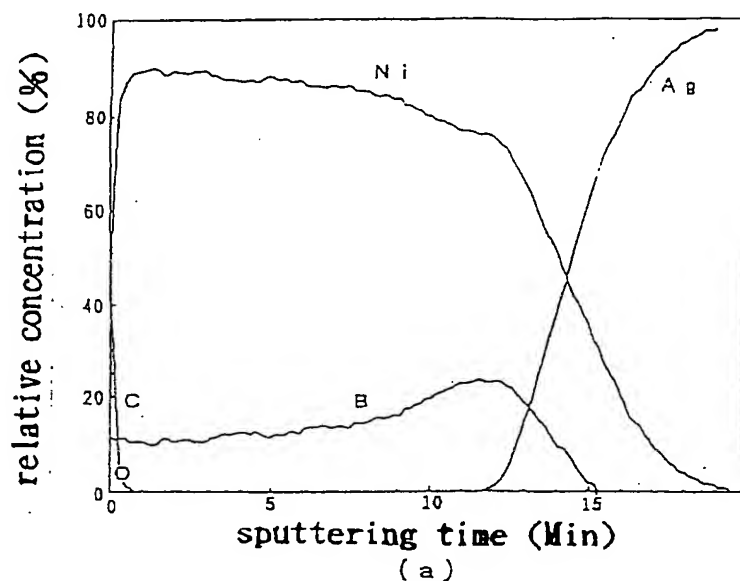
annealed for 50 min in Ar at 673K

incidence angle for thin film 5°

CuK $\alpha$   $\lambda = 1.54\text{\AA}$ 



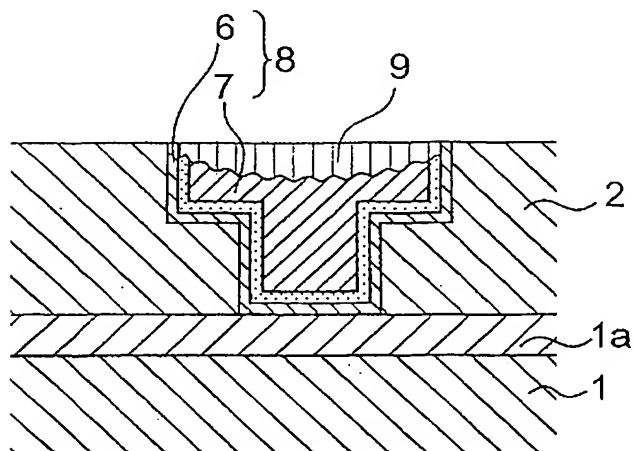
results of analysis of the surface of the annealed Ni-B alloy film



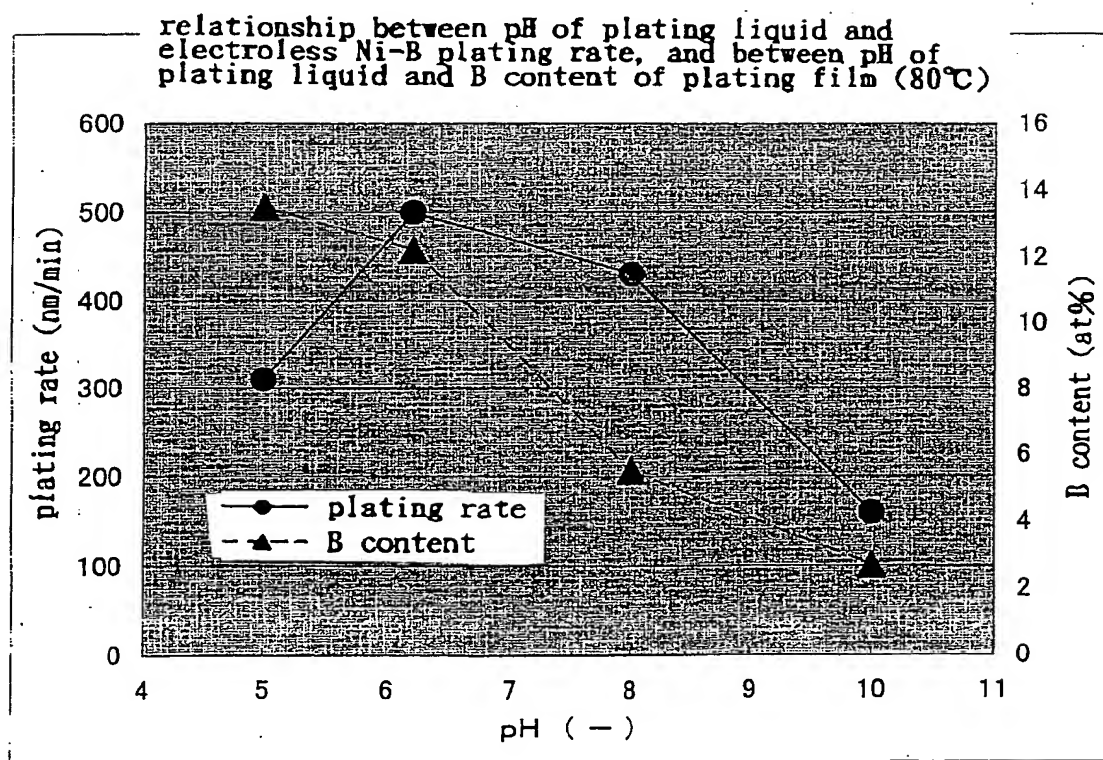
results of analysis of the surface of the annealed Ni-B alloy film

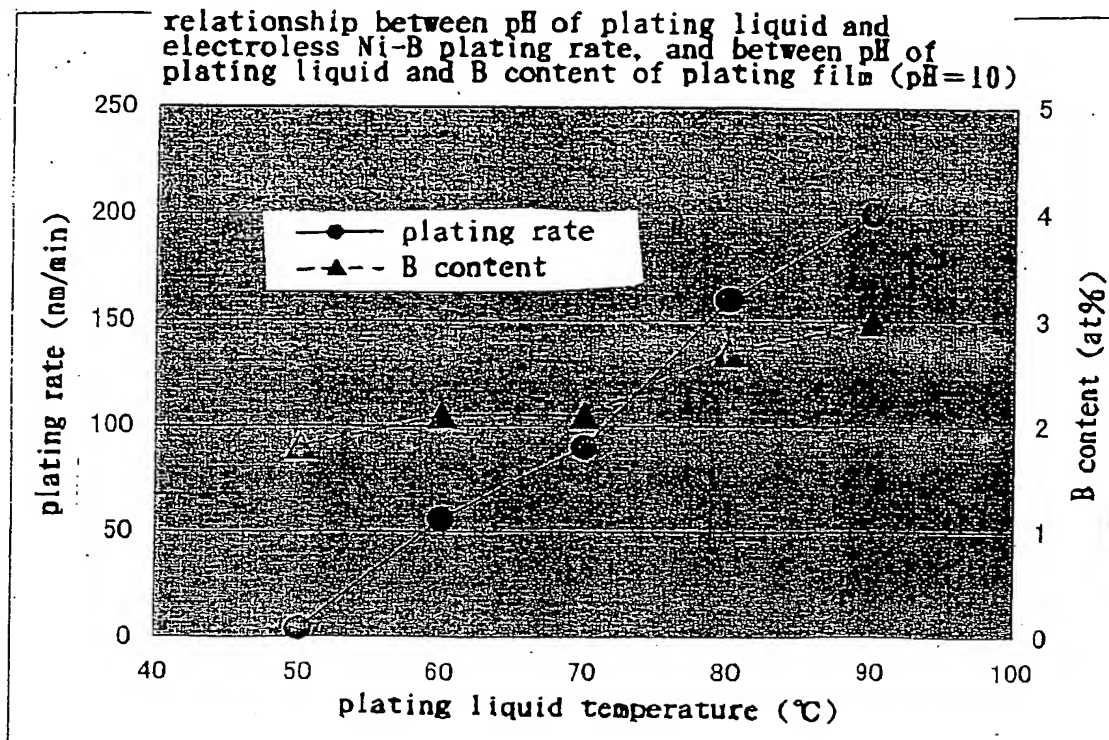
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(FIG. 8)

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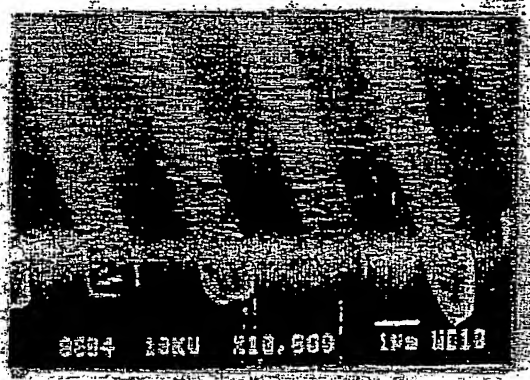
(FIG. 9)



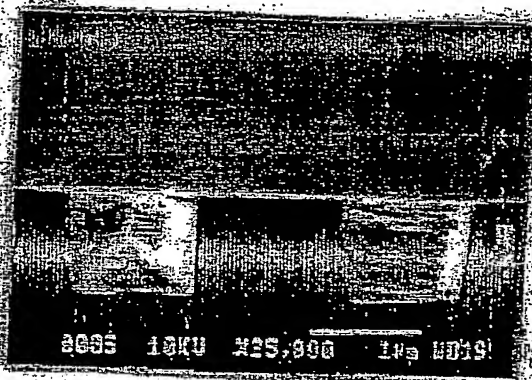


(FIG. 11)

(a)



(b)



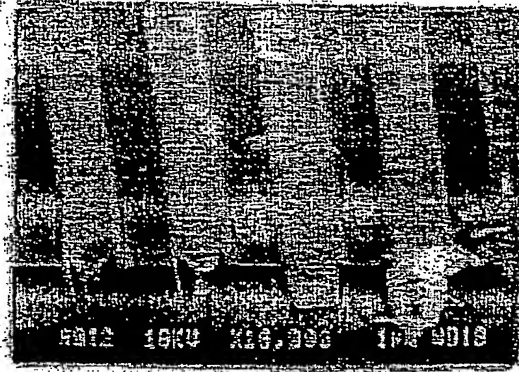


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(FIG. 12)

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(a)



(b)

